MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

Reactions of Mono(disilylamino)phosphines

with Carbon Tetrachloride

by

R.R. Ford, M.A. Goodman, R.H. Neilson
A.K. Roy, U.G. Wettermark, P. Wisian-Neilson

Prepared for Publication

in

Inorganic Chemistry

Texas Christian University
Chemistry Department
Fort Worth, TX 76129

May 18, 1984

B

AD-A141 628

DTIC FILE COPY

DTIC
ELECTE
MAY 29 1984
S   D

84 05 29 005

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER TCU/DC/TR-84-02	2. GOVT ACCESSION NO. AD-A141 628	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* Reactions of Mono(disilylamino)phosphines with Carbon Tetrachloride	5. TYPE OF REPORT & PERIOD COVERED Technical Report, 1983	
	6. PERFORMING ORG. REPORT NUMBER TR-84-02	
7. AUTHOR(s) R.R. Ford, M.A. Goodman, R.H. Neilson A.K. Roy, U.G. Wettermark, P. Wisian-Neilson	8. CONTRACT OR GRANT NUMBER(s) N00014-79-C-0632	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Texas Christian University Fort Worth, TX 76129	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-052-720	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research	12. REPORT DATE May 18, 1984	
	13. NUMBER OF PAGES 26	
14. MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)*	15. SECURITY CLASS. *(of this report)*	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

Prepared for publication in <u>Inorganic Chemistry</u>

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

phosphine   P-chlorophosphoranimine
phosphoranimine   N-silylphosphoranimine
(silylamino)phosphine

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

See Attached

A series of mono(disilylamino)phosphines $(Me_3Si)_2NPRR'$ (R, R' = Me, Et, $\underline{i}$-Pr, $\underline{t}$-Bu, CH_2SiMe_3, $CH_2CH=CH_2$, CH_2Ph, Ph, NMe_2, OMe, OCH_2CF_3) and two related phosphines, $Me_2SiCH_2CH_2Me_2SiNP(\underline{t}$-Bu)$CH_2SiMe_3$ and $(\underline{t}$-$BuMe_2Si)_2NPMe_2$, were treated with CCl_4 either neat or in CH_2Cl_2. The reactions proceeded with elimination of $CHCl_3$ and/or Me_3SiCCl_3 to form a variety of new P-chloro-N-silylphosphoranimines of general formula $Me_3SiN=P(Cl)R'R''$. The preferential course of the reaction was dependent on solvent polarity and on the electronic and steric influence of the substituents at nitrogen and phosphorus. Complete physical and spectroscopic (^1H, ^{13}C, and ^{31}P NMR) characterization data are given for the new phosphines and P-chloro-N-silylphosphorani-mines.

Accession For	
NTIS GRA&I	✓
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	

Dist	Avail and/or Special
A-1	

DTIC
COPY
INSPECTED
?

Contribution from the

Department of Chemistry

Texas Christian University

Fort Worth, TX 76129

Reactions of Mono(disilylamino)phosphines with Carbon Tetrachloride[1]

Randal R. Ford, Mary A. Goodman, Robert H. Neilson,

Aroop K. Roy, Urszula G. Wettermark, and Patty Wisian-Neilson*

A series of mono(disilylamino)phosphines $(Me_3Si)_2NPRR'$ (R,
R' = Me, Et, $\underline{i}$-Pr, $\underline{t}$-Bu, CH_2SiMe_3, $CH_2CH=CH_2$, CH_2Ph, Ph, NMe_2,
OMe, OCH_2CF_3) and two related phosphines, $Me_2SiCH_2CH_2Me_2SiNP(\underline{t}$-
Bu)CH_2SiMe_3 and $(\underline{t}$-$BuMe_2Si)_2NPMe_2$, were treated with CCl_4 either
neat or in CH_2Cl_2. The reactions proceeded with elimination of
$CHCl_3$ and/or Me_3SiCCl_3 to form a variety of new P-chloro-N-
silylphosphoranimines of general formula $Me_3SiN=P(Cl)R'R''$. The
preferential course of the reaction was dependent on solvent
polarity and on the electronic and steric influence of the
substituents at nitrogen and phosphorus. Complete physical and
spectroscopic (^1H, ^{13}C, and ^{31}P NMR) characterization data are
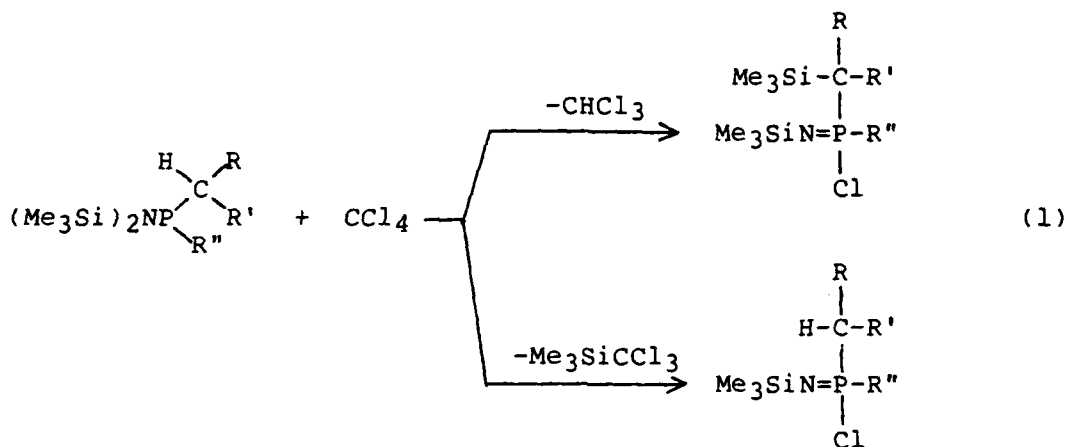given for the new phosphines and P-chloro-N-silylphosphorani-
mines.

Introduction

Due to the reactivity of the silicon-nitrogen bond, the chemistry of (disilylamino)phosphines, i.e. $(Me_3Si)_2NPRR'$, often differs substantially from that of simple alkyl or aryl substituted phosphines.[2] As part of our continuing study of the reactivity of silicon-nitrogen-phosphorus compounds, we have investigated the oxidation reactions of a variety of bis(disilylamino)phosphines[3] and mono(disilylamino)phosphines with CCl_4.

The reaction of CCl_4 with tertiary phosphines which contain a CH proton α to phosphorus, but no disilylamino groups, produces $CHCl_3$ and phosphorus ylides.[4] This presumably occurs via initial formation of an ion pair intermediate $[R_3PCl^+][CCl_3^-]$[5] with subsequent attack at the hydrogen by the CCl_3^- anion.

It was shown earlier that an alternate reaction pathway also becomes important when CCl_4 interacts with phosphines containing both an α hydrogen and two disilylamino groups.[3] In addition to proton abstraction by the CCl_3^- anion, attack at a silicon-nitrogen bond may occur with elimination of Me_3SiCCl_3. The competition between these two pathways is influenced by the steric bulk of the substitutents at phosphorus and by solvent polarity.

In this paper, we report on the reactions of CCl_4 with mono(disilylamino)phosphines which contain α hydrogens. As in the reactions of CCl_4 with bis(disilylamino)phosphines, both the silicon-nitrogen bond and the α hydrogens are potentially

reactive sites. Two different types of N-silylphosphoranimine products may, therefore, be produced from these reactions (eq 1).

$$(Me_3Si)_2NP\underset{R''}{\overset{H\diagdown\diagup R}{\underset{\diagup}{C}}}{}_{R'} \; + \; CCl_4 \; \longrightarrow \; \begin{array}{c} \xrightarrow{\;-CHCl_3\;} \quad \begin{array}{c} R \\ | \\ Me_3Si-C-R' \\ | \\ Me_3SiN=P-R'' \\ | \\ Cl \end{array} \\[3em] \xrightarrow{\;-Me_3SiCCl_3\;} \quad \begin{array}{c} R \\ | \\ H-C-R' \\ | \\ Me_3SiN=P-R'' \\ | \\ Cl \end{array} \end{array} \qquad (1)$$

Our primary objectives were (a) to compare the CCl_4 reaction products with those obtained from bis(disilylamino)phosphines or from tertiary phosphines with no disilylamino substituents, (b) to better understand the influence of steric and electronic differences of substituents at phosphorus, i.e. R, R', and R", and (c) to prepare various P-chloro-N-silylphosphoranimines which are potential precursors to polyphosphazenes and to novel three-coordinate phosphorus compounds.

Results and Discussion

Phosphine Synthesis. The various bis(disilylamino)-phosphines used in this study can be divided into four general categories: (1) simple dialkyl- or alkyl(phenyl)phosphines (1-7); (2) (trimethylsilylmethyl)phosphines (8-14); (3) phosphines with

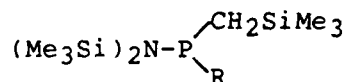benzyl or allyl substituents (15-18); and (4) systems with N-silyl groups other than Me_3Si (19-20).

$(Me_3Si)_2N-P\begin{smallmatrix}R\\R'\end{smallmatrix}$
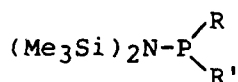
1: R = R' = Me

2: R = R' = Et

3: R = R' = i-Pr

4: R = i-Pr, R' = t-Bu

5: R = Ph, R' = Me

6: R = Ph, R' = Et

7: R = Ph, R' = i-Pr

$(Me_3Si)_2N-P\begin{smallmatrix}CH_2SiMe_3\\R\end{smallmatrix}$

8: R = Me

9: R = CH_2SiMe_3

10: R = Ph

11: R = t-Bu

12: R = OMe

13: R = OCH_2CF_3

14: R = NMe_2

$(Me_3Si)_2N-P\begin{smallmatrix}CH_2R\\R'\end{smallmatrix}$
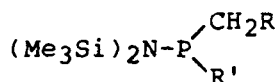
15: R = Ph, R' = Ph

16: R = Ph, R' = CH_2Ph

17: R = $CH=CH_2$, R' = Ph

18: R = $CH=CH_2$, R' = $CH_2CH=CH_2$

$\begin{bmatrix}Me_2\\Si\\Si\\Me_2\end{bmatrix}N-P\begin{smallmatrix}CH_2SiMe_3\\t-Bu\end{smallmatrix}$

19

$(t-BuMe_2Si)_2N-P\begin{smallmatrix}Me\\Me\end{smallmatrix}$
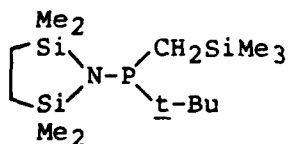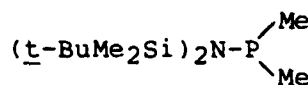
20

Many of these phosphines were prepared as described previously using the Wilburn procedure[6] or related methods.[7,8]

Of the compounds reported here for the first time, phosphines 8 and 13 were prepared by the nucleophilic substitution reactions of MeMgBr or CF_3CH_2OH with $(Me_3Si)_2NP(Cl)CH_2SiMe_3$.[8] Compound 10 was made from $(Me_3Si)_2NP(Cl)Ph$[6] and Me_3SiCH_2MgCl.[9] Repeated distillations failed to give an analytically pure sample of 10, but a satisfactory analysis was obtained for 23, the P-chloro-N-silylphosphoranimine derivative obtained from its reaction with CCl_4. The preparation of the dimethylamino compound 14[10] involved the sequential reaction of $Me_3SiCH_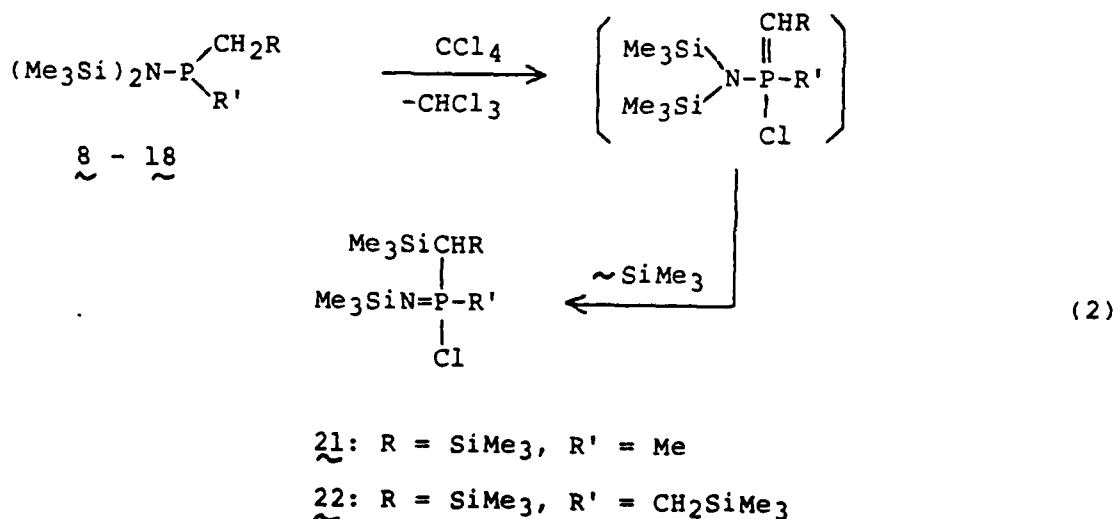2PCl_2$ with Me_3SiNMe_2 and $LiN(SiMe_3)_2$. Allyl and benzyl Grignard reagents were used in the Wilburn synthesis[6] to prepare phosphines 15-18. Compounds 15, 16, and 17, each had broad boiling point ranges and failed to give satisfactory elemental analysis. As in the case of 10, however, the trace impurities in these phosphines were not detectable in their NMR spectra. Moreover, good analytical data were obtained for the P-chloro-phosphoranimine derivatives 28 and 29, the decomposition product of 31, and several other derivatives[11]. Compounds 19 and 20 were made by procedures similar to those above using $(t-BuMe_2Si)_2NH$[12] and $Me_2SiCH_2CH_2SiMe_2NH$[13] in place of $(Me_3Si)_2NH$.

Preparative and ^{31}P NMR spectral data for these new compounds are listed in Table II. The ^{1}H and ^{13}C NMR data for selected compounds is given in Table I with complete spectral and analytical data included as Supplementary Material. The ^{1}H NMR spectra of several compounds (8, 10, 13, 15, and 16) show that the CH_2 protons of the CH_2SiMe_3 and CH_2Ph groups are

diastereotopic. The splitting pattern of these protons is a typical AB portion of an ABX spectrum (X = ^{31}P). Standard procedures for analysis of an ABX spectrum[14] were used to determine the chemical shifts and coupling constants. The ^{1}H NMR spectra of phosphines 17-19 could not be analyzed in detail since the patterns were significantly complicated by the signals of other CH and/or CH$_2$ protons.

CCl_4 Reactions. The reactions of mono(disilylamino)-phosphines with carbon tetrachloride are grouped into two general categories: (a) those which result only in elimination of CHCl$_3$ and (b) those which proceed with elimination of both CHCl$_3$ and Me$_3$SiCCl$_3$. These groups are discussed independently below.

a) CHCl$_3$ Elimination. Despite the presence of the disilylamino group on phosphorus, a large number of phosphines with α hydrogens were found to react with CCl$_4$ in the same manner as tertiary alkyl phosphines[4] giving only CHCl$_3$ elimination (eq 2). Unlike simple tertiary phosphines, however, the products

$$(Me_3Si)_2N-P{\overset{\displaystyle CH_2R}{\underset{\displaystyle R'}{}}} \quad \xrightarrow[-CHCl_3]{CCl_4} \quad \left(\begin{array}{c} Me_3Si \\ \\ Me_3Si \end{array} \overset{\displaystyle CHR}{\overset{\displaystyle \|}{N-\underset{\displaystyle Cl}{\overset{\displaystyle |}{P}}-R'}} \right)$$

$$\underset{\sim}{8} - \underset{\sim}{18}$$

$$\overset{\displaystyle Me_3SiCHR}{\underset{\displaystyle Cl}{\overset{\displaystyle |}{Me_3SiN=P-R'}}} \quad \xleftarrow{\sim SiMe_3} \qquad\qquad (2)$$

$$\underset{\sim}{21}: R = SiMe_3, R' = Me$$

$$\underset{\sim}{22}: R = SiMe_3, R' = CH_2SiMe_3$$

23: R = SiMe$_3$, R' = Ph

24: R = SiMe$_3$, R' = $\underline{t}$-Bu

25: R = SiMe$_3$, R' = OMe

26: R = SiMe$_3$, R' = OCH$_2$CF$_3$

27: R = SiMe$_3$, R' = NMe$_2$

28: R = R' = Ph

29: R = Ph, R' = CH$_2$Ph

30: R = CH=CH$_2$, R' = Ph

31: R = CH=CH$_2$, R' = CH$_2$CH=CH$_2$

are P-chloro-N-silylphosphoranimines and not phosphorus ylides.
The ylides are presumably intermediates which undergo a rapid
[1,3] silyl shift from nitrogen to carbon to form the N-silyl-
phosphoranimines 21-31. There is precedence for such a silyl
shift in a number of related systems.[3,15] Several features of
the ^{1}H and ^{13}C NMR spectra of the products indicated that the
phosphoranimines, rather than the ylides, were indeed obtained.
In fact, none of these compounds exhibited the upfield chemical
shifts typical of ylides in either the ^{1}H or ^{13}C NMR spectra (^{1}H,
ca. -0.8 ppm and ^{13}C, ca. -7.0 ppm).[16] The presence of a
(Me$_3$Si)$_2$CH group in compounds 21-27 is indicated by the
observation of three Me$_3$Si signals in the ^{1}H NMR. One signal is
the imino group, Me$_3$SiN=, and the others are the C-bonded
diastereotopic Me$_3$Si groups adjacent to a chiral phosphorus.
Evidence for the non-equivalence of the two Me$_3$Si groups on
carbon is provided by the chemical shift changes of these signals
which occur upon changing the solvent from benzene to CH$_2$Cl$_2$.

The observation of two distinct Me$_3$Si signals in the ^{1}H and ^{13}C NMR spectra as well as the lack of typical ylide signals is consistent with the phosphoranimine structures for 28 and 29. In addition, the P-C-H signals in the ^{1}H and ^{13}C NMR spectra of 30 and 31 had large J$_{PH}$ (13-18 Hz) and J$_{PC}$ (80-83 Hz) couplings as well as ^{1}H NMR chemical shifts indicative of allylic (2-3 ppm), rather than vinylic (5-6 ppm) protons[17]. Two signals were observed in the ^{31}P NMR spectra of 28-31 due to the diastereomers which result from the presence of two chiral centers in these molecules.

With the exception of compound 30, derived from the allyl(phenyl)phosphine 17, these new phosphoranimines were isolated and purified by vacuum distillation. They were identified by NMR spectroscopy and also characterized by elemental analysis. Compound 30 was a high boiling material which was best purified by recrystallization, after which NMR spectra indicated that very little impurity remained. Attempted distillation of the purified material resulted in decomposition via elimination of Me$_3$SiCl. The residue after heating was identified as $\left\{[CH_2=CH-C(SiMe_3)H]P(Ph)=N\right\}_n$ by elemental analysis and ^{31}P NMR (see Experimental Section).

Two related phosphines, 19 and 20, with different silyl substituents at nitrogen also reacted with CCl$_4$ to produce only CHCl$_3$ elimination products (eq 3 and 4). The seven-membered ring compound 32 is analogous to that obtained from a similar [1,3]
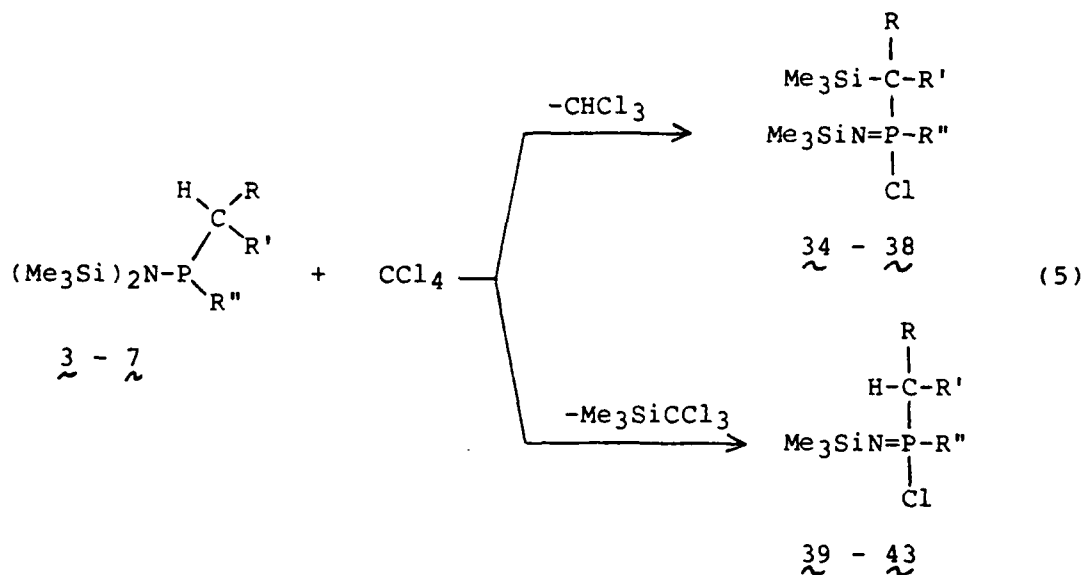
$$\text{(3)}$$

$$\text{(4)}$$
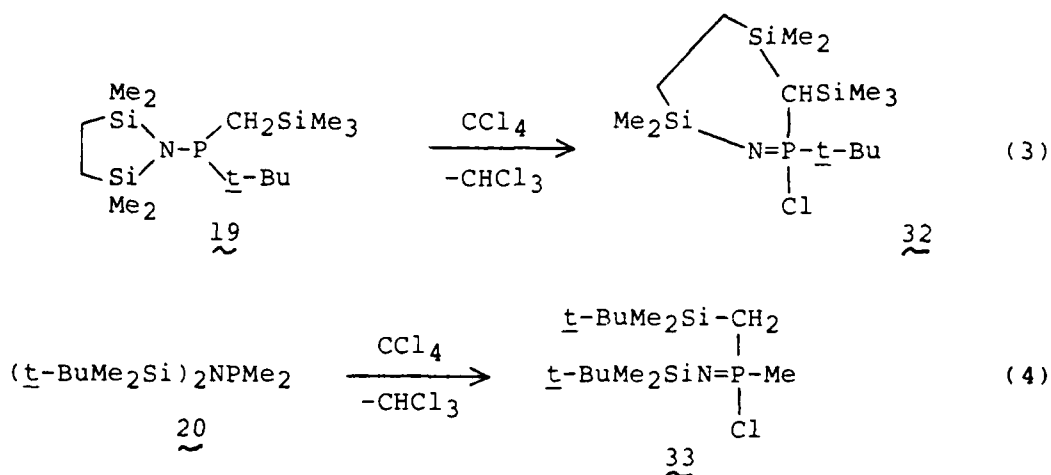
silyl shift upon treatment of $Me_2SiCH_2CH_2Me_2SiNPMe_3^+ \ I^-$ with

$\underline{n}$-BuLi.[15] As noted in this earlier case, the formation of the

cyclic compound strongly suggests that the silyl shift from

nitrogen to carbon is an intramolecular process. The reaction of

$\underline{20}$ with CCl_4 (eq 4) is also consistent with the process being

intramolecular. In contrast to $(Me_3Si)_2NPMe_2$ ($\underline{1}$), which is

discussed later, $\underline{20}$ gives exclusively the $CHCl_3$ elimination

product $\underline{33}$ either with CH_2Cl_2 as a solvent or in excess CCl_4.

Presumably the conformation of the bulky $\underline{t}$-butyl group prevents

the external attack of the CCl_3^- anion at silicon [which readily

occurs with less hindered groups in $(Me_3Si)_2NPMe_2$], but does not

interfere with an internal attack at silicon by an ylidic carbon

within the same molecule.

A common feature in most of the phosphines involved in these

reactions is the acidic character of the α protons. Attack of

the CCl_3^- anion on these protons is likely because the resulting

ylide intermediates are resonance stabilized by the adjacent

SiMe$_3$, CH=CH$_2$, or Ph groups. Once formed, the ylides may then easily rearrange via a [1,3] silyl shift. We have noted only a few exceptions to this generalization. As reported previously,[3] [(Me$_3$Si)$_2$N]$_2$PCH$_2$R (R = SiMe$_3$, Ph) reacted with CCl$_4$ to give both CHCl$_3$ and Me$_3$SiCCl$_3$ elimination products. Formation of Me$_3$SiCCl$_3$ in these cases is not surprising since there are a large number of Me$_3$Si groups available for attack by the CCl$_3^-$ anion. Another exception occurred in this series. The reaction of (Me$_3$Si)$_2$NP(CH$_2$SiMe$_3$)Me (8) in CH$_2$Cl$_2$ produced only the CHCl$_3$ elimination product 21, but in excess CCl$_4$ with no other solvent, another phosphorus compound was also formed as indicated by ^{31}P NMR (δ 25.5). Although it was not possible to separate this second product from 21, NMR analysis indicated that the CCl$_3^-$ anion may also have attacked the hydrogens on the P-Me group.

(b) CHCl$_3$ and Me$_3$SiCCl$_3$ Elimination. The reactions of mono(disilylamino)phosphines containing simple alkyl groups (i.e. Me, Et, i-Pr) with CCl$_4$ were often more complicated. Generally, both CHCl$_3$ and Me$_3$SiCCl$_3$ elimination products were formed (eq 5) with a change in solvent having a profound effect on which products were predominant. This is in contrast to most of the reactions described above where only CHCl$_3$ elimination was observed in either CH$_2$Cl$_2$ or in excess CCl$_4$. Table III summarizes the yields of each type of product obtained when these reactions were done in CH$_2$Cl$_2$ and in excess CCl$_4$.

$$\text{(Me}_3\text{Si)}_2\text{N-P} \quad \begin{array}{c} \text{H} \diagdown \diagup \text{R} \\ \text{C} \\ \diagup \diagdown \text{R'} \\ \text{R''} \end{array} \quad + \quad \text{CCl}_4 \quad \xrightarrow[]{} \quad \begin{array}{c} \xrightarrow{-\text{CHCl}_3} \quad \begin{array}{c} \text{R} \\ | \\ \text{Me}_3\text{Si-C-R'} \\ | \\ \text{Me}_3\text{SiN=P-R''} \\ | \\ \text{Cl} \end{array} \\ \\ \underset{\sim}{34} - \underset{\sim}{38} \\ \\ \xrightarrow{-\text{Me}_3\text{SiCCl}_3} \quad \begin{array}{c} \text{R} \\ | \\ \text{H-C-R'} \\ | \\ \text{Me}_3\text{SiN=P-R''} \\ | \\ \text{Cl} \end{array} \\ \\ \underset{\sim}{39} - \underset{\sim}{43} \end{array} \qquad (5)$$
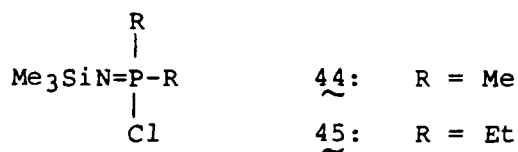
$$\underset{\sim}{3} - \underset{\sim}{7}$$

When these reactions were carried out neat (i.e. excess CCl_4), the favored products were always those resulting from the elimination of CHCl_3 ($\underset{\sim}{34}$-$\underset{\sim}{38}$). For reasons similar to those discussed above, these products were identified by NMR spectroscopy as the P-chloro-N-silylphosphoranimines and not the ylides. Unlike many of the previous reactions, at least trace amounts of the $\text{Me}_3\text{SiCCl}_3$ elimination products were observed in each reaction mixture.

When the same phosphines were treated with CCl_4 in CH_2Cl_2, the product distribution was influenced by the nature of the phosphorus substituent. The iso-propylphosphines ($\underset{\sim}{3}$, $\underset{\sim}{4}$, and $\underset{\sim}{7}$) produced small amounts of the CHCl_3 elimination products and large yields of the $\text{Me}_3\text{SiCCl}_3$ elimination products, $\underset{\sim}{41}$-$\underset{\sim}{43}$. In these cases the CCl_3^- anion which is relatively free in the polar
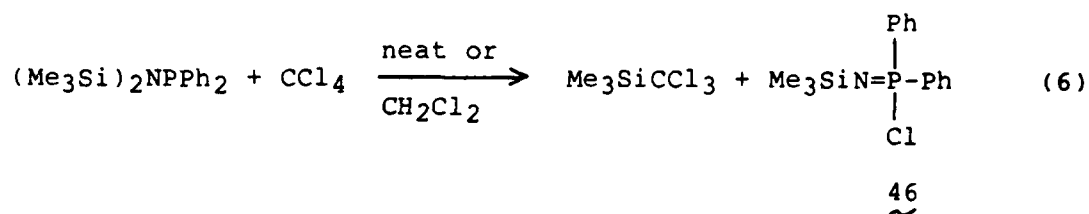
solvent CH_2Cl_2, preferentially attacks the silicon rather than the sterically hindered hydrogens in the iso-propyl group. The Ph/Me and Ph/Et phosphines 5 and 6, on the other hand, produced primarily the $CHCl_3$ elimination products, 34 and 35. Here the hydrogens of the methyl and ethyl groups are less sterically crowded so there is less competition by the Me_3Si group for the CCl_3^- anion.

The reactions of the simplest phosphines $(Me_3Si)_2NPR_2$ (1: R = Me, 2: R = Et) gave complex mixtures of products either in CH_2Cl_2 or CCl_4. Typically, as many as four major signals were observed in the ^{31}P NMR spectra of the reaction mixtures. When each reaction was carried out under very dilute conditions (<0.5M in CH_2Cl_2), low yields of the Me_3SiCCl_3 elimination products, 44 and 45 were isolated by distillation. No other pure compounds

$$
\begin{array}{c}
\hspace{2em} R \\
\hspace{2em} | \\
Me_3SiN{=}P{-}R \\
\hspace{2em} | \\
\hspace{2em} Cl
\end{array}
\qquad
\begin{array}{l}
44: \quad R = Me \\[1em]
45: \quad R = Et
\end{array}
$$

could be isolated from any of the reaction mixtures. In view of the clean reaction (eq 4) observed for the analogous $(t\text{-}BuMe_2Si)_2N$ substituted phosphine 20, these results show that the nature of the silicon substituents can also significantly influence the course of such reactions.

One reaction of CCl_4 with a mono(disilylamino)phosphine with no α hydrogens was also investigated (eq 6). As expected, the

$$(Me_3Si)_2NPPh_2 + CCl_4 \xrightarrow[CH_2Cl_2]{neat\ or} Me_3SiCCl_3 + Me_3SiN=\overset{\overset{\displaystyle Ph}{|}}{\underset{\underset{\displaystyle Cl}{|}}{P}}-Ph \qquad (6)$$

46

Me_3SiCCl_3 elimination product 46 was obtained. On heating in a sealed glass ampoule, 46 eliminated Me_3SiCl forming $(Ph_2PN)_3$. This is analogous to the thermal decomposition of $Me_3SiN=P(X)Ph_2$ $(X = F[18], Br[19])$.

Conclusion. Several trends become evident from the results of this series of reactions as well as those involving bis(disilylamino)phosphines. Both the elimination of $CHCl_3$ and Me_3SiCCl_3 are reasonable pathways for these reactions to follow. The elimination of $CHCl_3$ is favored by (a) non-polar solvents which promote a "tighter" intermediate ion pair $[R_3PCl^+][CCl_3^-]$, resulting in preferential attack of the CCl_3^- anion on the nearby α hydrogen; (b) substituents at the α carbon (e.g. $SiMe_3$, Ph, $CH=CH_2$) which tend to resonance stabilize the ylide intermediate; and (c) α hydrogens which are not sterically hindered by other substituents on the α carbon. The elimination of Me_3SiCCl_3 is favored by (a) polar solvents which allow for a relatively "loose" ion pair and a CCl_3^- anion which is free to attack a peripheral Me_3Si group; (b) an abundance of $(Me_3Si)_2N$ groups[3] so there is a greater chance for attack at silicon; and (c) sterically hindered α hydrogens which limit their accessibility by the CCl_3^- anion.

Experimental Section

General Procedures. The following reagents were purchased from commercial sources and used without further purification: MeMgBr(Et_2O), PhCH$_2$MgCl(THF), t-BuLi(pentane), CH$_2$=CHCH$_2$MgCl(Et_2O), CF$_3$CH$_2$OH, and PhPCl$_2$. Spectroscopic grade CCl$_4$ was stored over molecular sieves. Dichloromethane, Et_2O, and Et_3N were distilled from CaH$_2$ prior to use. Published procedures were used to prepare Me$_2$SiCH$_2$CH$_2$Me$_2$SiNH[13], Me$_3$SiCH$_2$MgCl[9], (Me$_3$Si)$_2$NLi[6], and (t-BuMe$_2$Si)$_2$NH[12]. The mono(disilylamino)phosphines, 1-7, 9, 11 and 12 were also prepared by published procedures.[6-8] Proton NMR spectra were recorded on a Varian-EM390 spectrometer, while a JEOL FX-60 spectrometer was used to record $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Table I contains ^1H and ^{13}C NMR data for representative compounds. Physical, preparative, and ^{31}P NMR data for all the compounds reported here are listed in Table II.

All reactions and manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. Typical procedures used in the preparation of the new compounds in this report are described below.

Preparation of (Me$_3$Si)$_2$NP(Me)CH$_2$SiMe$_3$, 8. The chlorophosphine (Me$_3$Si)$_2$NP(Cl)CH$_2$SiMe$_3$[8] (31.08 g, 99 mmol) and Et_2O (100 mL) were placed in a three-necked, round bottom flask equipped with a magnetic stir bar, a nitrogen inlet, and an addition funnel. The reaction flask was cooled to 0°C and MeMgBr (36.7

ml, 2.7 M, 99 mmol) was added dropwise via the addition funnel. The mixture was allowed to warm to room temperature and to stir overnight. The Grignard salts were removed from the mixture by filtration under nitrogen and solvent was removed from the filtrate under reduced pressure. Distillation of the yellow liquid residue through a 10 cm Vigreux column yielded 19.0 g of a colorless liquid which was identified as $\underline{8}$.

Preparation of $(Me_3Si)_2NP(OCH_2CF_3)CH_2SiMe_3$, 13. A three-necked round bottom flask equipped with a magnetic stir bar, a nitrogen inlet, and a septum was charged with $(Me_3Si)_2NP(Cl)CH_2SiMe_3$[8] (18.4 g, 58.6 mmol), Et_3N (8.2 mL, 58.8 mmol), and Et_2O (50 mL). The mixture was cooled to 0^oC and CF_3CH_2OH (4.6 mL, 58.6 mmol) was added slowly via syringe. This mixture was warmed to room temperature and stirred for ca. 2 h. Filtration under nitrogen removed $Et_3N\cdot HCl$. Solvent was removed from the filtrate affording a colorless residue which was distilled under vacuum through a 10 cm Vigreux column to give 16.1 g of $\underline{13}$ as a colorless liquid.

Preparation of $(Me_3Si)_2NP(Ph)CH_2SiMe_3$, 10. A three-necked, round bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and an addition funnel was charged with $PhPCl_2$ (27.2 mL, 0.20 mol) and Et_2O (100 mL) and the mixture was cooled to -78^oC. A solution of $(Me_3Si)_2NLi$ (0.20 mol in ca. 200 mL of hexane[6]) was added dropwise via the addition funnel. The mixture was then warmed to 0^oC; stirred at that temperature for 2 h; then warmed to room temperature and stirred overnight. This mixture was

cooled to 0° and Me_3SiCH_2MgCl[9] (0.20 mol in ca. 200 mL of Et_2O) was added dropwise. After warming to room temperature and stirring for ca. 5 h, the mixture was filtered under nitrogen. Solvent removal at reduced pressure gave a yellow residue which was distilled through a 10 cm Vigreux column to give 43.3 g of a colorless liquid which solidified on standing (mp 30-31°C) and was identified as 10.

Preparation of $Me_2SiCH_2CH_2Me_2SiNP(t\text{-Bu})CH_2SiMe_3$, 19. A procedure similar to that used to prepare $(Me_3Si)_2NP(Cl)CH_2SiMe_3$[8] was used to prepare $Me_2SiCH_2CH_2Me_2SiNP(Cl)CH_2SiMe_3$[10]. This chlorophosphine (19.8 g, 63.5 mmol) and Et_2O (50 mL) were placed in a three-necked, round bottom flask equipped with a nitrogen inlet, a magnetic stir bar, and a septum. After cooling the solution to 0°C, t-BuLi (32.0 mL, 2M) was added via syringe. The mixture was warmed to room temperature and stirred overnight. Filtration, solvent removal from the filtrate, and distillation of the residue gave 19.

Synthesis of 15, 16, 17, 18, and 20 by the Wilburn Method. Typically 250 to 350 mmol of 15-18 were prepared according to the Wilburn[6] procedure using $PhCH_2MgCl$ or $CH_2=CHCH_2MgCl$. Compound 20 was also prepared by the Wilburn procedure using $(t\text{-BuMe}_2Si)_2NH$ in place of $(Me_3Si)_2NH$.

Reactions of (Disilylamino)phosphines with CCl_4. Unless otherwise noted, the following procedures are typical of those used to prepare the P-chloro-N-silylphosphoranimines 21-46.

a) Neat Reactions. The (disilylamino)phosphine $\underset{\sim}{3}$ (6.60 g, 23.8 mmol) was placed in a 100-mL round bottom flask equipped with a magnetic stir bar, nitrogen inlet, and septum. After cooling to 0^oC, a five-fold excess (11.5 mL, 118.9 mmol) of CCl_4 was added to the phosphine via syringe. The mixture was stirred overnight at room temperature and a yellow solution formed. Excess CCl_4 and other volatiles were removed under reduced pressure. Vacuum distillation of the residue afforded $\underset{\sim}{37}$.

b) Reactions in CH_2Cl_2. In a similar set-up, the phosphine $\underset{\sim}{3}$ (4.86 g, 17.5 mmol) and CH_2Cl_2 (18 mL) were placed in the flask and cooled to 0^oC. One molar equivalent (1.7 mL, 17.5 mmol) of CCl_4 was then added via syringe. Solvent removal at reduced pressure and distillation of the yellow liquid residue gave $\underset{\sim}{42}$.

Reaction of 17 with CCl_4. The reaction was carried out as described in $\underline{a}$ and $\underline{b}$ above, but upon attempted distillation only a few drops distilled. When the reaction was repeated, the crude product was recrystallized from CH_2Cl_2 by adding hexane (Tables I and II). An attempt to further purify this material by vacuum distillation resulted in decomposition. The residue in the flask was identified as oligomeric $\left\{[CH_2=CHCH(SiMe_3)]P(Ph)=N\right\}_n$ by ^{31}P NMR (δ - 5.42) and elemental analysis: Calc. C, 61.24; H, 7.71. Found: C, 61.62; H, 6.70.

Reaction of 1 and 2 with CCl_4. The reaction of $\underset{\sim}{1}$ with CCl_4 was carried out as described in $\underline{a}$ and $\underline{b}$ above and also according

to procedure <u>b</u> with freshly distilled hexane as a solvent. In each case as many as 4 major signals and several smaller signals were observed in the ^{31}P NMR spectra of the reaction mixtures. Vacuum distillation did not give any fractions containing a single pure compound. However, low yields of pure samples of 44 and 45 were obtained in dilute CH_2Cl_2 solutions. Typically, the phosphine 1 (7.23 g, 32.7 mmol) and CH_2Cl_2 (32 mL) were placed in a 250 mL round bottom flask equipped with a magnetic stirrer, nitrogen inlet, and addition funnel. After cooling the solution to 0°C, CCl_4 (3.2 mL, 32.7 mmol) in CH_2Cl_2 (32 mL) was added dropwise. The mixture was warmed to room temperature and stirred for ca. one h. Solvent removal and distillation afforded 44. A similar procedure using ca. twice as much CH_2Cl_2 was used to obtain 45.

<u>Thermal decomposition of 46.</u> A sample (3.95 g, 12.8 mmol) of 46 was placed in a heavy-walled glass ampoule which was sealed under vacuum. Light brown solids formed after heating in an oven at 180°C for 67 h. The ampoule was opened and Me_3SiCl (1.38 g, yield 97%) was removed under vacuum. A ^{31}P NMR spectrum of the crude material contained a large signal at 15.24 and a small one at δ 6.12. Recrystallization from hot CH_3CN gave pure crystals of the trimer $(Ph_2P=N)_3$ (mp 228-230°C, $^{31}P(THF) \delta 15.9)$[20].

Supplementary Material Available. Tables of ^{1}H and ^{13}C NMR spectroscopic data and analytical data for all new compounds. Ordering information is given on any current masthead page.

References

1. (a) Wisian-Neilson, P.; Ford, R.R.; Li, B.-L.; Neilson, R.H. "Abstracts of Papers", 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 1982, American Chemical Society: Washington, DC, 1982; INORG 147. (b) Ford, R.R.; Goodman, M.A.; Li, B.-Li; Neilson, R.H.; Roy, A.K.; Wettermark, U.G.; Wisian-Neilson, P.; Xie, Z.-M. XVII Organosilicon Symposium, Fargo, ND, June 1983.

2. Morton, D.W.; Neilson, R.H. Organometallics 1982, 1, 289 and references sited therein.

3. Li, B.L.; Engenito, J.S., Jr.; Neilson, R.H.; Wisian-Neilson, P. Inorg. Chem. 1983, 22, 575.

4. (a) Appel, R.; Peters, J.; Schmitz, R. Z. Anorg. Allg. Chem. 1981, 18, 475. (b) Kolodiazhnyi, O.I. Tetrahedron Lett. 1980, 21, 3983.

5. Appel, R. Angew. Chem. Int. Ed. Engl 1975, 14, 801.

6. Neilson, R.H.; Wisian-Neilson, P. Inorg. Chem. 1982, 21, 3568.

7. O'Neal, H.R.; Neilson, R.H. Inorg. Chem. 1983, 22, 814.

8. Neilson, R.H. Inorg. Chem. 1981, 20, 1679.

9. Andersen, R.A.; Wilkinson, G. Inorg. Synth. 1979, 19, 262.

10. Thoma, R.J.; Neilson, R.H., unpublished results.

11. Roy, A.K.; Neilson, R.H.; Wisian-Neilson, P., unpublished results.

12. West, R.; Boudjouk, P. _J_. _Am_. _Chem_. _Soc_. 1973, _95_, 3983.

13. Baney, R.H., Haberland, G.G. _J_. _Organomet_. _Chem_. 1966, _5_, 320.

14. Becker, E.D. "High Resolution NMR"; Academic Press: New York, 1969; p. 152.

15. Wilburn, J.C.; Neilson, R.H. _Inorg_. _Chem_. 1979, 18, _347_.

16. Schmidbaur, H.; Buchner, W.; Scheutzow, D. _Chem_. _Ber_. 1973, _106_, 1251.

17. Morton, D.W.; Neilson, R.H. _Organometallics_ 1982, _1_, 623.

18. Wisian-Neilson, P.; Neilson, R.H.; Cowley, A.H. _Inorg_. _Chem_. 1977, _16_, 1460.

19. Wisian-Neilson, P.; Neilson, R.H. _Inorg_. _Chem_. 1980, _19_, 1875.

20. Allcock, H.R. "Phosphorus-Nitrogen Compounds," Academic Press: New York, 1972.

Table I: ^{1}H and ^{13}C NMR Spectroscopic Data for Selected Compounds.[a]

compd	signal	^{1}H NMR			^{13}C NMR	
		δ	J_{PH}	J_{HH}	δ	J_{PC}
$(Me_3Si)_2NP$ $\big\backslash$ CH_2SiMe_3 / OCH_2CF_3 **13**	$(Me_3Si)_2N$	0.32	1.5		4.55	8.6
	$\underline{Me}_3SiCH_2$	0.15	0.9		0	4.9
	$Me_3Si\underline{CH}_2$	0.88	7.3	13.8	27.41	39.1
		1.75	1.8	13.8		
	$O\underline{CH}_2CF_3$	3.93	7.2[c]		65.50	23.2[c]
	$OCH_2\underline{CF}_3$				124.38	13.4[d]
$(Me_3Si)_2NP$ $\big\backslash$ $CH_2CH=CH_2$ / $CH_2CH=CH_2$ **18**	$(Me_3Si)_2N$	0.37[e]	1.2		4.79	7.3
	$-\underline{CH}_2CH=CH_2$	2.27–2.91[b,e]			38.03	23.8
	$-CH_2\underline{CH}=CH_2$	5.63–6.17[b,e]			134.23	12.8
	$-CH_2CH=\underline{CH}_2$	4.94–5.27[b,e]			116.44	10.4
$Me_3SiN=P-CH(SiMe_3)_2$ with Cl and OCH_2CF_3 **26**	Me_3SiN	0.08			2.90	5.5
	$(\underline{Me}_3Si)_2CH$	0.24			1.81	4.3
		0.31				
	$(Me_3Si)_2\underline{CH}$	1.31	27.0		27.71	100.7
	$O\underline{CH}_2CF_3$	4.20	8.4[f]		60.69	7.3[g]
	$OCH_2\underline{CF}_3$				123.48	14.7[h]

Table I. continued

compd	signal	^1H NMR			^{13}C NMR	
		δ	J_{PH}	J_{HH}	δ	J_{PC}
Cl SiMe$_3$ | | Me$_3$SiN=P—CHCH=CH$_2$ | CH$_2$CH=CH$_2$ **31**	Me$_3$SiN	−0.02	0.6		3.29	4.9
	Me$_3$SiCH	0.21 0.22			0.69 0.85	2.4 2.4
	Me$_3$SiCH	2.3–3.0[b]			45.87 43.17	80.0 80.6
	SiCHCH=CH$_2$	4.7–5.4[b,e]			132.22 131.82	7.3 8.5
	SiCHCH=CH$_2$	5.5–6.1[b,e]			120.81 120.63	14.7 14.0
	PCH$_2$CH=CH$_2$	2.3–3.0[b]			44.37 44.13	70.2 70.2
	PCH$_2$CH=CH$_2$	4.7–5.4[b,e]			128.93 128.53	10.4 9.8
	PCH$_2$CH=CH$_2$	5.5–6.1[b,e]			117.80 118.21	17.1 15.9
SiMe$_2$ ... CHSiMe$_3$ Me$_2$Si N=P-t-Bu Cl **32**	MeSi	0.01–0.38[b]			1.17–5.52[b]	
	Me$_3$SiCH	1.56	13.8		25.24	32.2
	SiCH$_2$	0.64–0.97[b]			11.50	
					12.93	
	Me$_3$C	1.19	19.2		25.40	
	Me$_3$C				40.45	88.9

Table I. continued

compd	signal	^{1}H NMR δ	J_{PH}	J_{HH}	^{13}C NMR δ	J_{PC}
Me$_3$SiN–P–CMe$_2$SiMe$_3$ (Cl above P, i-Pr below) **37**	Me$_3$SiN	0.18			3.43	4.3
	Me$_3$SiC	0.03			-1.46	
	Me$_3$Si$\underline{C}$				32.04	65.9
	Me$_2$C	1.08–1.41^b			20.99	4.9
					20.79	1.3
	Me$_2$CH	1.08–1.41^b			19.51	3.1
					18.76	3.7
	Me$_2$$\underline{C}$H	2.05–2.41^b			34.90	71.4
Me$_3$SiN=P–i-Pr (Cl above P, i-Pr below) **42**	Me$_3$SiN	0.02			3.37	4.9
	Me$_2$CH	1.20	19.2	6.8	16.43	3.1
					16.00	3.7
	Me$_2$$\underline{C}$H	2.19	6.9	6.9	32.45	78.1

$\underline{a}$ Chemical shifts downfield from Me$_4$Si for ^{1}H and ^{13}C spectra, coupling constants in Hz. Solvents: ^{1}H, CH$_2$Cl$_2$; ^{13}C, CDCl$_3$, unless noted otherwise. $\underline{b}$ Multiplet. $\underline{c}$ J_{HF} = 9.0 Hz; J_{FC} = 35.4 Hz. $\underline{d}$ J_{FC} = 278.3 Hz. $\underline{e}$ Solvent: benzene. $\underline{f}$ Couplings in benzene; J_{FH} = 8.4 Hz. $\underline{g}$ J_{FC} = 37.2 Hz. $\underline{h}$ J_{FC} = 277.7 Hz.

Table II. Preparative and ^{31}P NMR Spectroscopic Data

| compd | preparative | | ^{31}P NMR |
	% yield[a]	bp °C(mm)	δ [b]
8	66	37-38(0.01)	36.29
10	61	98-100(0.01)	41.95
13	73	40-42(0.01)	165.49
15	78	115-150(0.05)	54.36
16	62	133-143(0.10)	62.53
17	65	73-90(0.02)	46.96
18	65	71-73(0.03)	49.61
19	56	65-69(0.01)	56.66
20	75	70-76(0.05)	31.21
21	76	51(0.01)	26.97
22	(71)	69-75(0.01) mp 38-41°C	29.06
23	(61)	82-86(0.01)	19.66
24	84	75-80(0.03)	49.71
25	(82)	48(0.01)	15.16
26	(78)	66-68(0.01)	12.13
27	(75)	61-62(0.01)	21.80
28	84	124-126(0.05)	18.58, 16.93[c]
29	(87)	130-137(0.05)	22.62, 24.03[c]
30	75[d]	104(0.05)[e]	17.72, 16.48[c]
31	(84)	70-78(0.15)	25.53, 23.40[c]
32	(62)	80-80.5(0.01)	52.14, 44.17[c]

Table II. continued

33	(72)	80–82(0.03)	23.53
34	(80)	77–81(0.10)	16.63
35	(82)	118(0.10)	25.80, 27.04[c]
36	(33)	92(0.03)	35.94
37	(75)	62(0.07)	54.01
38	(52)	70–72(0.07)	57.42
40	8	87–96(1.3)	24.03
41	82	68–70(0.01)	30.63
42	77	38(0.15)	50.77
43	95	38–40(0.05)	54.55
44	28	46–47(4.7)	23.05
45	42	60–61(1.2)	39.07
46	(74)	110(0.05)	11.30

[a] Values in parentheses are yields from neat CCl_4 reactions. Other yields for 21–46 are from CCl_4 reactions in CH_2Cl_2. [b] Chemical shifts downfield from H_3PO_4.

Solvent: $CDCl_3$. [c] Diastereomers. [d] Estimated yield from recrystallization. [e] Only a few drops distilled before decomposition.

Table III.   Percent Yields of Products Obtained via Equation 5[a]

R	R'	R"	$CHCl_3$ elimination			Me_3SiCCl_3 elimination		
			No.	neat	CH_2Cl_2	No.	neat	CH_2Cl_2
H	H	Ph	34	80	79	39	t	t
Me	H	Ph	35	82	25	40	t	8
Me	Me	Ph	36	33	t	41	12	82
Me	Me	i-Pr	37	75	t	42	t	77
Me	Me	t-Bu	38	52	t	43	31	95

[a] Isolated yields, based on starting phosphine, of products obtained by fractional distillation. t = trace (i.e. product not isolated by distillation but detected by ^{31}P NMR in the reaction mixture).

END

DATE
FILMED

7-84

DTIC